EFFECT OF THERMO-MECHANICAL PROCESSING AND AGING ON THE STRESS CORROSION CRACKING RESISTANCE OF ALLOY 690

Milestone Report
March 31, 2016

EXECUTIVE SUMMARY

This final milestone report covers the stress corrosion cracking (SCC) results of Alloy 690 after different thermal-mechanical processing (TMP) and aging treatments obtained since our report in September. These research efforts focus on the microstructural and mechanical property changes induced by the aging treatments and the possible effects of those changes on the SCC susceptibility of this material in simulated PWR primary water environments. A single heat of Alloy 690 (Ni-30Cr-9Fe) was produced by the Korean Atomic Energy Research Institute (KAERI). Results are summarized as follows:

1. Aging treatments at 350 °C and 550 °C resulted in decreased yield strength (YS) and SCC susceptibility of solution annealed and cold rolled samples. The reduction in YS is expected due to the softening caused by recovery of the dislocation substructure and appears to also reduce SCC susceptibility. Conversely, aging at 475 °C, while also reducing YS, resulted in what appears to be a significant increase in SCC susceptibility. This appears to be related to the effects of carbide precipitation on high angle grain boundaries (HABs) and prior coherent twin boundaries (PCTBs) at 475 °C vs. 350 °C or 550 °C.

2. For thermally treated and cold rolled samples (TTCR) aged at 350 °C and 475 °C, the yield strength also decreased with increasing aging time and temperature. However, unlike the non-thermally treated material, aging appears to lead to decreased SCC susceptibility as measured by such things as crack density, average crack length and crack length per unit area. This appears to be related to (a) the slightly lower yield stresses of the TT material under comparable conditions (CR, CR+350 °C and CR+475 °C) and/or (b) the damage that occurs during cold rolling due to the carbides formed during the thermal treatment.

3. Coherent annealing twin boundaries were observed to lose coherency during cold rolling in both solution annealed + cold rolled (CR) and thermally treated + cold rolled (TTCR) samples. These will be referred to as previously coherent twin boundaries (PCTBs) for the duration of this report. These PCTBs were determined to be susceptible to carbide precipitation during aging, as well as to cracking during SCC testing, due to their increased boundary energies. Such twin boundary cracking was rare in samples that were not CR prior to SCC testing.

4. For unaged conditions, TTCR had lower SCC susceptibility than the CR material presumably due to a beneficial effect of the carbides that formed on random high angle boundaries (HABs) during the thermal treatment. However, it is also noted that there is approximately a 5% lower YS in the TTCR material may play a significant role in this difference in SCC susceptibility.

5. For the aged conditions, the relative SCC susceptibility of PCTBs in the CR samples is larger than that for TTCR samples, perhaps because the HABs and PCTBs in the TTCR samples are less affected by the aging treatments due to preexisting carbides.

6. CR samples aged at 550 °C for 10,000 h underwent precipitation of both carbides and α-Cr at both HABs and PCTBs. The carbides formed as isolated precipitates as well as cellular discontinuous product. The α-Cr formed as isolated precipitates as well as in recrystallized colonies at HABs.

7. The effects of testing technique, and therefore the state of stress/strain at the crack tip, are important considerations in the SCC testing of Alloy 690. Thus, comparisons of results from SSRT and constant K tests are difficult. Furthermore, the YS differences make it challenging to compare

the behavior of SA and CR conditions, as well as CR and CR+Aged conditions in some cases where aging results in significant changes in strength either locally (partial recrystallization) or globally (recovery and softening).

1.0 ALLOY NOTATION

The notation for various TMP and aging conditions of Alloy 690 is detailed in below in Table 1.

Table 1: Explanation of abbreviated sample nomenclature. Note, all conditions were first given the solution anneal treatment.

Abbrev.	Meaning	Specifics
SA	Solution Annealed	1100 °C - 1 hour
TT	Thermally Treated	700 °C - 17 hours
CR	Cold Rolled	20% reduction
TTCR	Thermally Treated then Cold Rolled	TT then 20% CR

Using this table the sample nomenclature is as follows: AA-BB-CC, where AA is the TMP condition, BB is the aging temperature in degrees Celsius, and CC is the aging time in hours. Note that all specimens were solution annealed prior to TMP. As such, specimen TTCR-475-10000 (or TTCR-475-10k) was solution annealed at 1100 °C for 1 hour, thermally treated at 700 °C for 17 hours, cold rolled 20%, and subsequently aged at 475 °C for 10,000 hours.

2.0 INTRODUCTION

Alloy 690 has been widely used as a structural material in nuclear power plants because of its superior performance to Alloy 600. However, it is not immune to primary water stress corrosion cracking (PWSCC) and under some conditions the crack growth rate (CGR) of Alloy 690 can be as high as that of mill-annealed Alloy 600. Thus, further improving the understanding of its SCC behavior is of great importance. While it is generally accepted that grain boundary carbides are beneficial in suppressing the SCC process,[1] some researchers have indicated that grain boundary carbides can increase the SCC susceptibility of Alloy 690 in the cold worked condition.[2,3] Clearly, more research is needed to clarify the effects of carbides on the SCC susceptibility of this important alloy.

Concern has also been raised about the detrimental effects of cold work on the SCC susceptibility of Alloy 690. There are consistent results showing that cold work increases the SCC growth rate of Alloy 690.[2,4] The explanation for this acceleration is that the higher yield strength could increase the strain rate ahead of the crack tip.[5] What should also be considered is that cold work can change the microstructure of the material and affect the aging kinetics.

This research has been aimed at evaluating the SCC susceptibilities of both solution annealed and thermally treated Alloy 690 that was cold rolled (CR and TTCR, respectively) and then given various aging treatments. Unaged samples as well as samples aged at various times and temperatures were tested in a simulated primary water environment. The effects of cold work and aging treatments on SCC behavior have been investigated in some detail. In our September Milestone report, we indicated the following: "Given the nature of the results reported in this milestone report, there are clearly things that need to be investigated more carefully in order to understand crack initiation behavior in Alloy 690 as follows:"

1. Investigate further the effects of aging at 475 and 550 °C on carbide precipitation in the CR samples. Study how the changes of grain boundary structure are linked to SCC susceptibility.

2. Characterize the carbides formed on PCTBs for the TTCR samples during aging and compare these carbides with the preexisting carbides on HABs formed during the thermal treatment.
3. Determine the factors controlling SCC susceptibility including the relative importance of cold work, carbide or other precipitation, strain rate, environment, etc.

3.0 EXPERIMENTAL

3.1 Metallographic Preparation

Specimens were prepared for SEM and EBSD analysis by sectioning the bulk bar into 8 x 8 x 2 mm slices. Metallographic preparation included grinding to 1200 grit SiC, followed by polishing using 6, 3, and 1 μm diamond suspension. Specimens were then electropolished in a solution of 45% acetic acid, 45% methanol, and 10% perchloric acid at -30 °C, 30 V, 15 mA, for 15-30 s.

S/TEM preparation consisted of sectioning an 8 x 8 x 1 mm wafer using a low speed diamond saw, followed by grinding to 100-150 μm thick. Specimens were then punched into 3 mm discs, and twin-jet electropolished in a solution of 45% acetic acid, 45% methanol, and 10% perchloric acid at -30 °C, 30 V, and ~15 mA until perforation.

3.2 Stress Corrosion Cracking (SCC) Testing

Most cold rolled conditions of the KAERI heat have been evaluated for their SCC susceptibility. A list of conditions recently tested in this program is provided in Table 1. All samples were machined into tensile bars as shown in Figure 1. The gage section of each tensile bar was mechanically abraded to #4000 grit and then electropolished for 30 s at 30 V in a solution of 10 volume percent perchloric acid in methanol, which was maintained at -30 °C. Some coupons measuring around 8 x 8 x 4 mm were also prepared using the same procedure for grain boundary characterization and IG precipitate analysis.

Slow strain rate testing (SSRT) was used to strain the samples at $1x10^{-8}$ s^{-1} in 360 °C high purity water containing 18 $^{cc}/_{kg}$ H_2. After the straining tests, a JEOL JSM-6480 SEM was used to image more than 40 equally spaced areas at 1000X along the gage section. The images were examined for intergranular cracks. Crack lengths per unit area, crack density and average crack length were calculated based on the crack number and measured crack length. Among the three parameters, crack length per unit area provides the most complete description of SCC susceptibility. In addition, TEM and 3D atom probe tomography were used to provide complementary structural (diffraction) and atomic resolution.

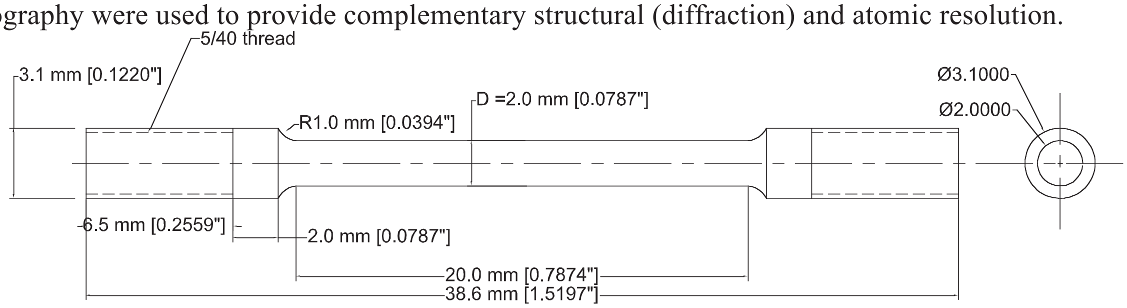


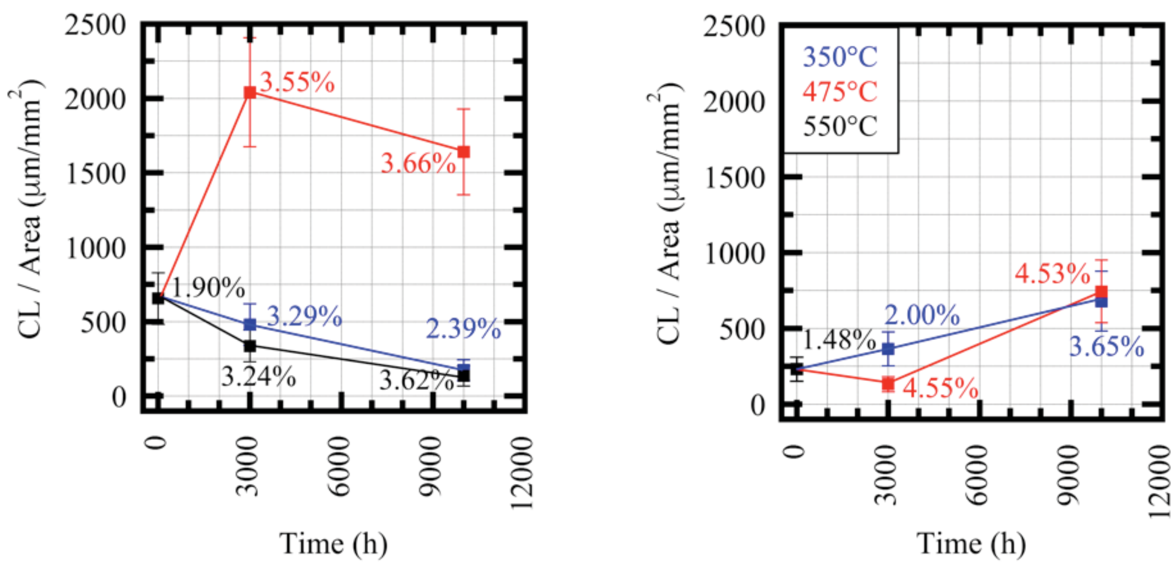
Figure 1: Tensile bar design used for the SCC tests.

4.0 RESULTS AND DISCUSSION

This section will be divided as indicated in the introduction based on our September milestone report.

4.1 Investigate further the effects of aging at 475 and 550 °C on carbide precipitation in the CR samples. Study how the changes of grain boundary structure are linked to SCC susceptibility.

As noted in the previous report, the CR+Aged samples displayed an unexpected behavior with respect to SCC cracking trends. Specifically, while softening due to recovery occurred during aging for all conditions, the cracking after aging at 475 °C increased, while that after aging at 350 °C and 550 °C decreased (Figure 2a). Likewise, the cracking in the TTCR plus aged samples did not exhibit this same sort of behavior (Figure 2b). In an effort to explain these differences, a more detailed analysis of the microstructures and properties was conducted.



(a) (b)

Figure 2: SCC statistics for (a) CR and (b) TTCR conditions of Alloy 690 after SSRT testing at 1x10^{-8} s^{-1} in 360 °C high purity water containing 18 $^{cc}/_{kg}$ H_2. Values of uniform strain for each condition are listed.

First of all, it has become clear in this work that cold work greatly influences SCC initiation in Alloy 690. Further, as shown by Bruemmer et al. (Figure 3), cold work also increases crack propagation considerably.[6,2,7,8] This appears to be related to the much higher yield stresses in the CR material (~200 MPa for SA material vs. ~800 MPa for CR material). Thus, the stress levels experienced by the material being tested at 360 °C under SSR conditions (or under constant K conditions) will be very different and, therefore, it makes little sense to compare the SCC properties (number of cracks, crack density, crack growth rate, etc.) of the CR and non-CR material. The implications of this will be discussed further below.

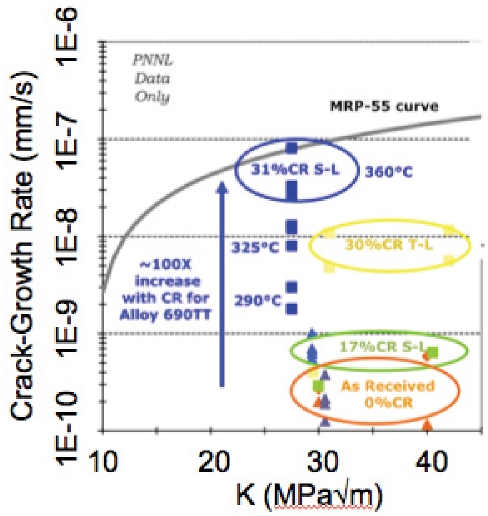


Figure 3: Crack growth data on Alloy 690 taken from the work by Bruemmer et al..[6,8] Note the significant influence of cold work on rate of crack propagation.

In an effort to explain the differences in behavior between the CR+Aged materials, it is important to discuss the effects of both the cold rolling and aging on the microstructural features that might influence cracking. First, as already mentioned, the cold rolling results in both considerable strain hardening of the material as well as damage to the coherent twin boundaries and their loss of coherency in many (most) cases. At 350 °C, although the driving force for both recovery and carbide precipitation is high, the kinetics are still quite low. This leads to slight recovery and limited carbide precipitation on both HABs and PCTBs. The softening lowers the stresses achieved during SCC testing and, since the carbides are small and sparsely distributed, they do not appear to have a significant influence on SCC initiation, i.e., the recovery plays the majority role in reducing crack initiation compared to the harder CR material.

At 475 °C, the kinetics are faster and the carbides develop much more significantly at both HABs and PCTBs. Thus, in spite of the greater recovery than that observed at 350 °C, a higher density of cracks initiate in this material suggesting that the brittle carbides play a significant role in crack initiation. Whether this is more of a chemical or a mechanical effect will be addressed further below.

At 550 °C, the increased kinetics lead to even greater amounts of recovery (softening) during aging. As seen in Figure 4, this softening leads to a reduction in YS of over 20% (~200 MPa) compared to the as CR condition. As in the 475 °C sample, the development of carbides is significant, as expected. However, unlike the 475 °C sample, there was a significant amount of α-Cr formation in small recrystallization colonies (concurrent α-Cr precipitation accompanying matrix recrystallization), as well as α-Cr formation at HABs. Thus, the combination of considerably greater softening due to recovery as well as local strain-free regions at the HABs and PCTBs leads to considerably different SCC behavior. Presumably, these soft pockets serve to lower the stresses that can develop at the grain boundaries even further than that expected from the bulk recovery/softening that occurs during aging. Representative SEM micrographs for the CR and CR+Aged conditions can be seen in Figure 5. Thus, it is not surprising that the cracking behavior is less in spite of the significant amount of second phases (carbides and α-Cr) that develop at the HABs and PCTBs. ThermoCalc (Figure 6) was used to determine at what temperatures α-Cr should form and it became clear that it does have a driving force for formation below about 600 °C. This implies that α-Cr also has a driving force to form at the lower aging temperatures but is presumably too sluggish for reasons that remain unclear.

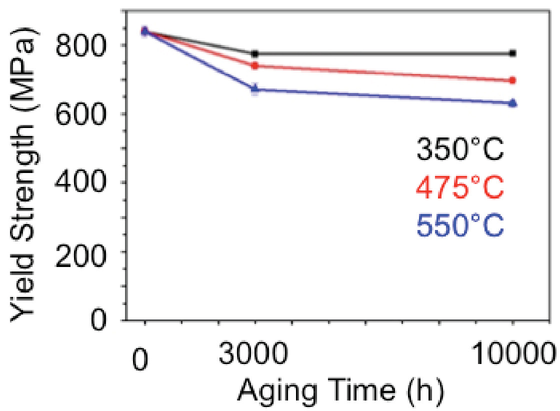


Figure 4: Yield strength for CR and CR+Aged conditions of Alloy 690 during SSRT testing at $1x10^{-8}$ s^{-1} in 360 °C high purity water containing 18 $^{cc}/_{kg}$ H_2

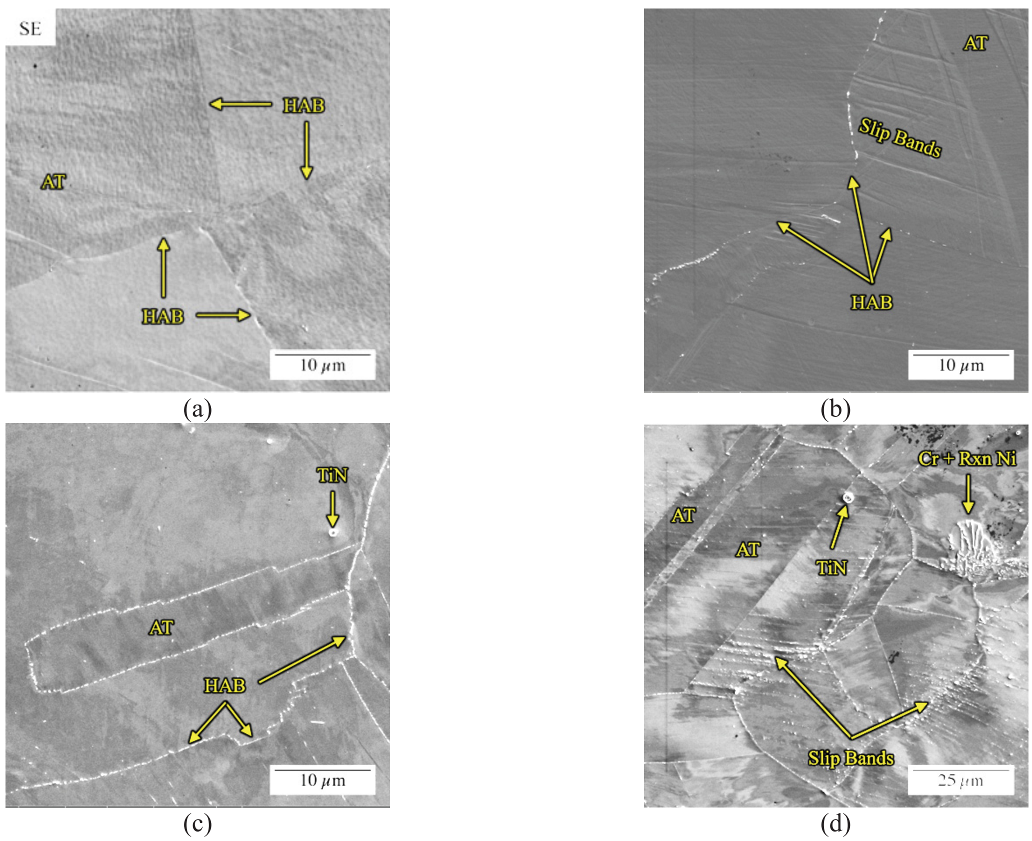


Figure 5: SEM micrographs of the Alloy 690 after solution annealing, cold rolling and aging for different times and temperatures: (a) CR-00-00 (b) CR-350-10k, (c) CR-475-10k, (d) CR-550-10k.

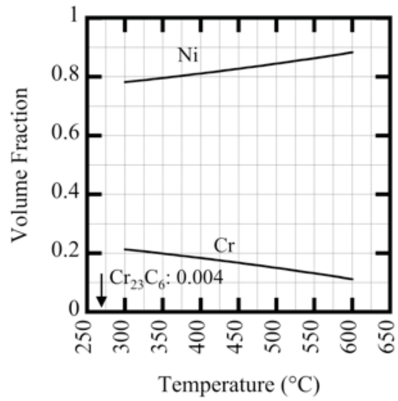


Figure 6: Results from ThermoCalc simulations indicating the stability of α-Cr below 600 °C. This is consistent with its formation during aging at 550 °C both as isolated particles as well as in the small recrystallization pockets observed.

As noted above, the cracking behavior of the TTCR material tended to be less than that of the CR material before and after aging. This appears to be related to the formation of grain boundary carbides upon the 700 °C thermal treatment and their damage during the CR process. Specifically, the $M_{23}C_6$ particles that form at 700 °C are considerably larger (200-400 nm) than those that form upon aging of the CR material at 475 °C and 550 °C (50-100 nm). Furthermore, during CR, some of the carbides crack and lead to void formation, as shown in Figure 7. Other differences are the slightly lower yield stresses of the TTCR material when compared to the CR material before and after aging. The lower yield stresses and the presence of cracked carbides and voids along grain boundaries clearly implies that these two factors may lower the stresses that are achieved during SCC testing and lead to fewer cracks at a given uniform strain. Further, it should be noted also that the driving force for carbide precipitation during aging should be reduced significantly given the large carbides that are already present after the TT. Thus, the development of carbides on the PCTBs is expected to be considerably less than in the CR material during aging – this will also impact the cracking behavior when compared with the CR material where the carbides develop more or less equally on the HABs and PCTBs.

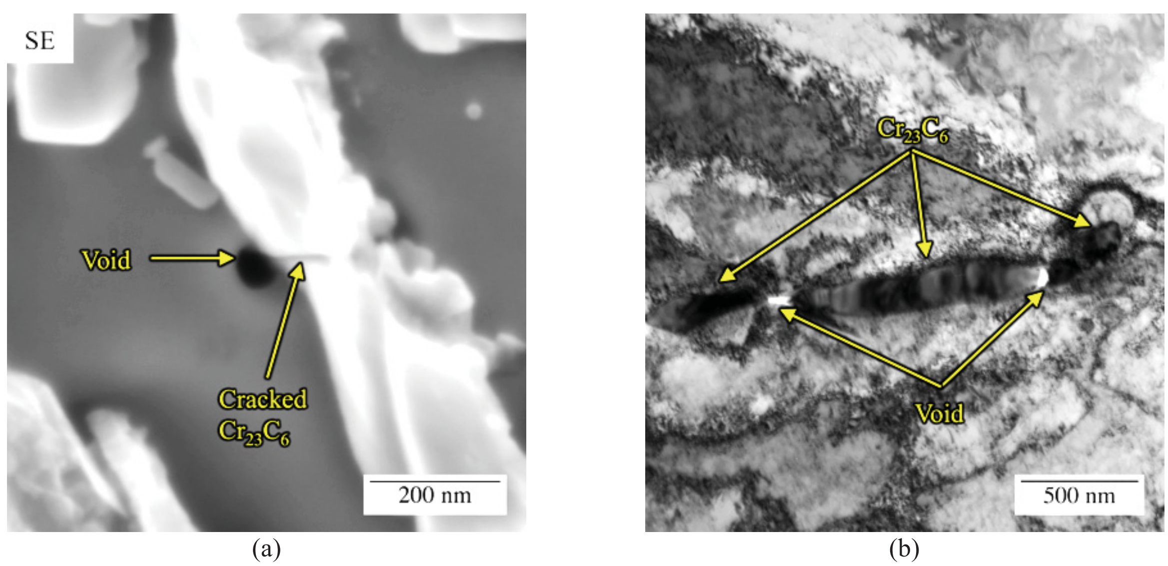


Figure 7: Analysis of grain boundary damage in TTCR-00-00, showing an (a) SEM micrograph of a cracked carbide and void formation in a cellular colony of $Cr_{23}C_6$, and (b) TEM image of voids forming between grain boundary carbides.

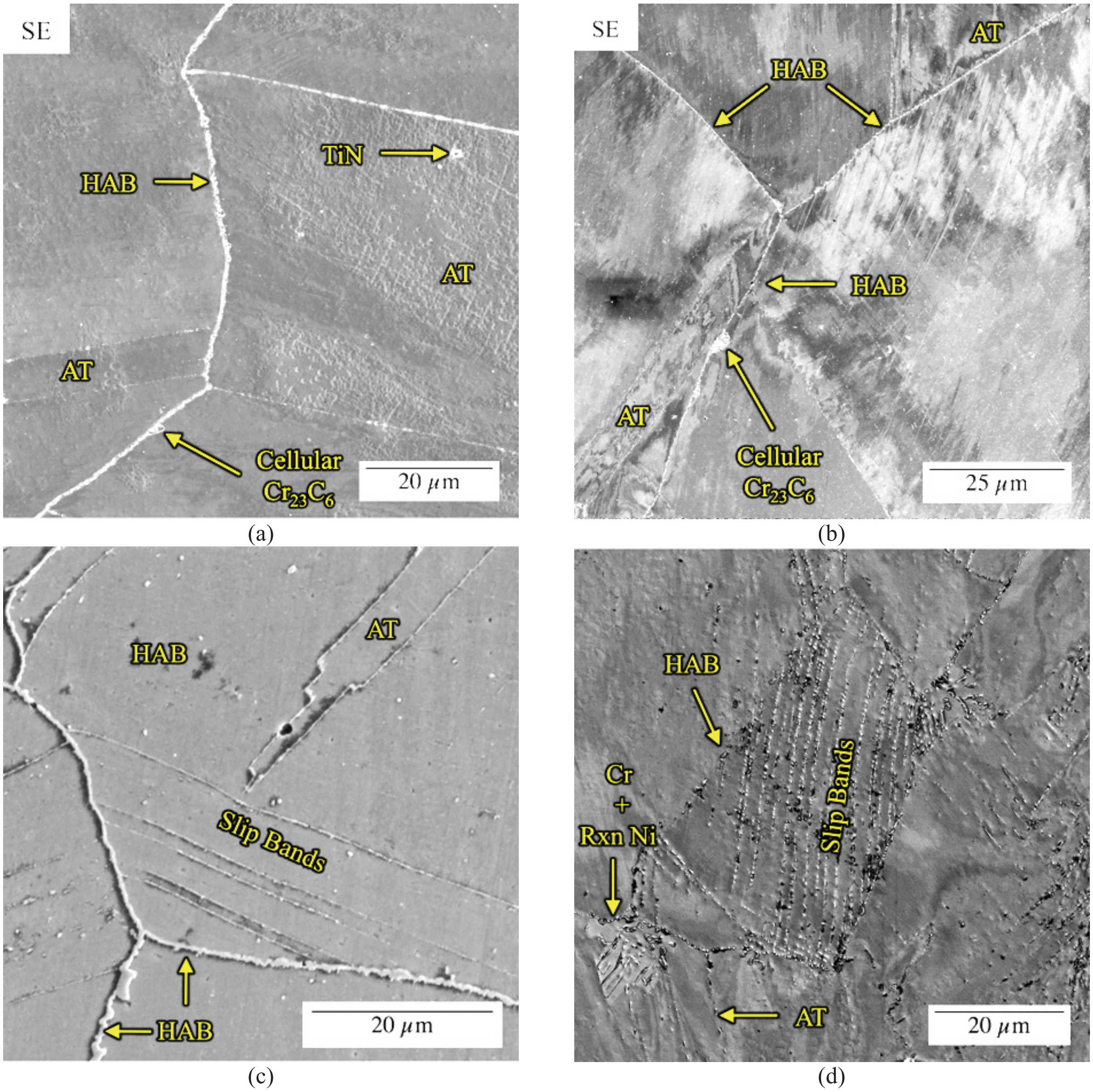
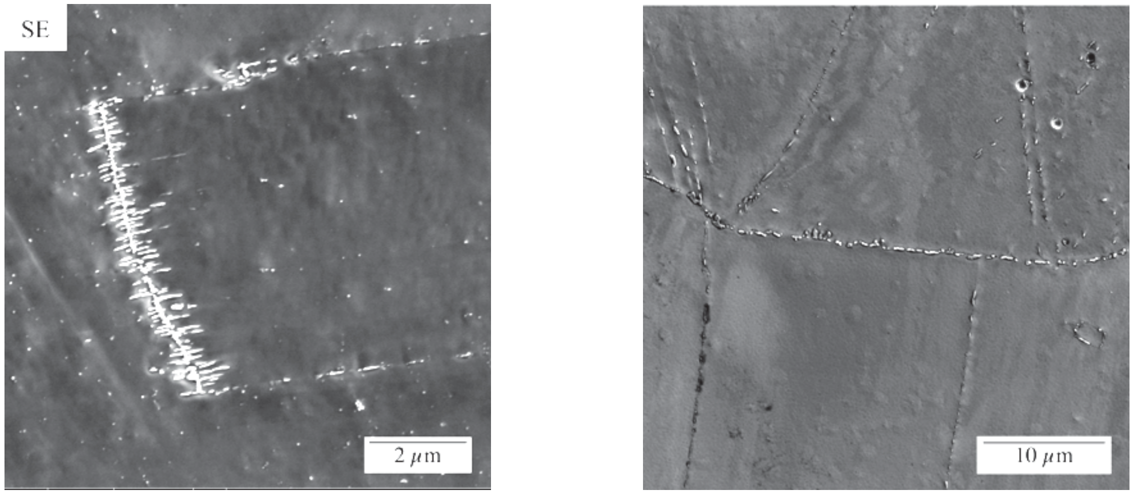


Figure 8: SEM micrographs of (a) TTCR-00-00, (b) TTCR-350-10k, (c) TTCR-475-10k and (d) TTCR-550-10k

4.2 Characterize the carbides formed on PCTBs for the TTCR samples during aging and compare these carbides with the preexisting carbides on HABs formed during the thermal treatment.

As pointed out in the previous section, the carbides that form on HAGBs upon thermal treatment are considerably larger than those that develop upon aging the CR material at 475 °C or 550 °C. Likewise, the formation of carbides during TT results in fewer carbides forming on PCTBs upon aging at 350 °C and 475 °C, as shown in Figure 9. Thus, it is not surprising that the density of SCC cracks is lower in the TTCR + aged material given that there are fewer boundaries decorated with carbides.



(a) (b)

Figure 9: SEM micrographs of carbide precipitation at PCTBs in (a) TTCR-00-00 and (b) TTCR-550-10k conditions of Alloy 690

4.3 Determine the factors controlling SCC susceptibility including the relative importance of cold work, carbide or other precipitation, strain rate, environment, etc.

Taken collectively, the results obtained in this study can be used to make certain conclusions regarding SCC susceptibility and the importance of the various factors mentioned. These will be mentioned in turn.

Cold Work – The current results indicate that one of the most important parameters is the amount of cold work in the material and how that influences the stress levels achieved during testing. The work by Bruemmer et al. has clearly shown that, at a given stress intensity, the crack velocity increases significantly with cold work.[2,6,7,9] The present results appear to be consistent with their results and indicate that the much higher yield stresses of the CR material has a significant influence on the SCC initiation behavior as well. Given how challenging it is to get Alloy 690 to undergo SCC initiation, it is fairly clear that avoiding significant CW should provide low SCC susceptibility. It is noted that the very significant work hardening due to CR results in a much smaller plastic zone size in the constant K tests by Bruemmer et al. (Figure 10).

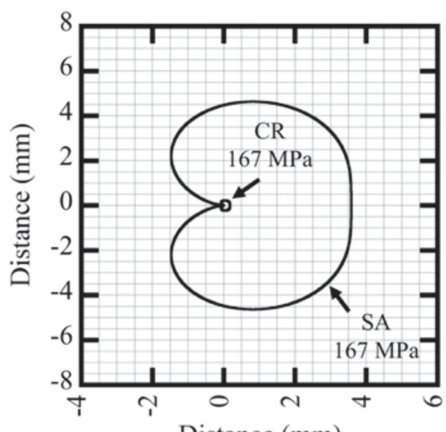


Figure 10: Crack tip plastic zones for a constant K SCC tests, using a 0.5CT geometry, a K_I of 30 MPa$\sqrt{m}$, and an initial crack length of 10.16 mm. Note the large difference in plastic zone size for the SA vs. the CR material.

Carbide and a-Cr Precipitation – As shown throughout this study, carbides may or may not influence SCC behavior. First of all, in the SA material with no cold work, the SCC cracking density determined after the SSR tests appears higher than that in the SA material that has been aged or thermally treated to form carbides. Thus, in the case of softer material, it appears that carbides are neutral or slightly beneficial to SCC behavior. However, when the material is cold worked, the carbides appear to increase SCC susceptibility especially when the material is not thermally treated prior to the CW + aging cycles. As the material softens due to recovery or local recrystallization, it is clear that the carbides have less of an effect on SCC.

Strain Rate and Environment – It is well known that slow strain rate testing in a corrosive environment of the type used in these studies is considered an extremely severe SCC test. This is simply related to the fact that more time is provided for any sort of environmental interaction to occur in the presence of stress/strain and if a material has any susceptibility to SCC, SSR testing will indicate its susceptibility. However, in the present study, while we were clearly able to show that crack initiation in 690 is possible in SSR tests, it is also clear that less severe tests will likely not lead to SCC. In fact, in the absence of significant cold work, it seems very unlikely that stresses of sufficient magnitude could easily be reached under normal loading conditions for this material in the different environments of interest to the nuclear industry**.**

CONCLUSIONS

1. Aging treatments at 350°C and 550°C decreased the yield strength and SCC susceptibility of solution annealed and cold rolled samples. This was explained by the softening caused by recovery of the dislocation substructure and appears to also reduce SCC susceptibility. Conversely, aging at 475°C significantly increased the SCC susceptibility although such treatments still induced softening of the material. It was proposed that the higher SCC susceptibility is related to the effects of carbide precipitation on both HAGBs and PCTBs.

2. For thermally treated and cold rolled samples (TTCR) aged at 350°C and 475°C, the yield strength decreased with increasing aging time and temperature due to recovery as expected. However, unlike the non-thermally treated material, the aging treatments at both temperatures decreased the SCC susceptibility. This is expected due to the recovery effects and the lack of significant precipitation during the aging treatments.

3. Coherent annealing twin boundaries lose coherency during cold rolling in both solution annealed and cold rolled (CR) and thermally treated and cold rolled (TTCR) samples. These PCTBs were determined to be susceptible to carbide precipitation during aging especially in the CR material where there was a higher driving force for carbide formation. In addition, these boundaries behave similar to HAGBs and undergo SCC, due to their increased boundary energies. Such twin boundary cracking was not observed in samples that were not CR and then aged.

4. For the unaged conditions, the TTCR material had lower SCC susceptibility than the CR material presumably because the amount of strain hardening and the yield stress was lower as was the amount of carbides that develop on the PCTBs.

5. Cold rolled samples aged at 550 °C for 10,000 h undergo precipitation of α-Cr, both as a concurrent recrystallization/precipitation producing colony-like structures and as isolated grain boundary precipitates. ThermoCalc was used to confirm the driving force for α-Cr at temperatures below 600 °C.

6. The effects of testing technique, and therefore the state of stress and strain at the crack tip, are crucial considerations in the SCC testing of Alloy 690. The different strength levels for the conditions of Alloy 690 that were investigated in this study have a significant influence on both crack initiation and propagation behavior and indicate that it is inappropriate to compare SA and

CR material before and after aging.

7. For the aged conditions, the relative SCC susceptibility of PCTBs in CR samples is larger than that for TTCR samples, perhaps because the HABs and PCTBs in the TTCR samples are less affected by the aging treatments due to preexisting carbides.
8. While SCC initiation is possible using SSRT, it seems highly unlikely that initiation in the parts used in power plants will occur unless there has been rather severe damage to the material for some reason.

5.0 REFERENCES

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